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Current status of hydrogen energy

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Abstract

This paper examines the present status of hydrogen energy and looks at different approaches for technological advances. Some of the new developments in the progress of the recent directions of world hydrogen production and utilization are reported.

The aim of this article is to inform the reader of hydrogen technology, economics, environmental impact, special system applications, hydrogen energy status around the world at the end of the 20 century as well as hydrogen organizations, associations, projects, periodicals and conferences. © 2002 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Fossil fuels possess very useful properties not shared by non-conventional energy sources (such as solar) that have made them popular during the last century. Unfortunately, fossil fuels are not renewable [1]. In addition, the pollutants emitted by fossil energy systems (e.g. CO, CO_2, C_nH_m, SO_x, NO_x, radioactivity, heavy metals, ashes, etc.) are greater and more damaging than those that might be produced by a renewable based hydrogen energy system [2]. Since the oil crisis of 1973, considerable progress has been made in the search for alternative energy sources. Although the water splitting process used to simultaneously generate hydrogen and oxygen has been demonstrated by the utilization of insolation, the technology is not mature enough to bring it to demonstration level. Much fundamental research remains to be done [3]. A long sought goal of energy research has been the search for a method to produce hydrogen fuel economically by splitting water using sunlight as the primary energy source.

One of the main domains of solar energy research concerns the development of a process for the production of solar fuels. Among the solar fuel candidates, hydrogen holds a pre-eminent position because of its high energy content, environmental compatibility and ease of storage and distribution. The different approaches for splitting water have been summarized by Bockris as follows: electrolysis, plasmolysis, magnetolysis, thermal approach (direct, catalytic and cyclic decomposition of water, as well as magmalysis), use of light (photosensitized decomposition using dyes, plasma-induced photolysis, photoelectrolysis, photo-aided electrolysis, the indirect path towards hydrogen by photoelectrolysis: the photoelectrochemical reduction of CO_2 and photovoltaic electrolysis), biocatalytic decomposition of water, radiolysis and other approaches [4].

Worldwide production of CO_2 emission to reduce the risk of climate change (greenhouse effect) requires a major restructuring of the energy system. The use of hydrogen as an energy carrier is a long term option to reduce CO_2 emissions. However, at the present time, hydrogen is not competitive with other energy carriers. The production costs of hydrogen from CO_2-free electricity (hydro, nuclear and solar) are typically 20–30 Ecu GJ^{-1} or more, which does not compare with todays oil and

gas prices of 5 Ecu GJ^{-1}. Fossil fuel conversion to hydrogen, with separation and storage of CO_2, might be an attractive transitional CO_2-free source of hydrogen at costs of 10–15 Ecu GJ^{-1}. A scenario study has been reported incorporating a complete set of new technologies (including hydrogen production) to reduce CO_2 emissions by the year 2040 [5].

Global utilization of fossil fuels for energy needs is rapidly resulting in critical environmental problems throughout the world. Energy, economic and political crises, as well as the health of humans, animals and plant life, are all critical concerns. There is an urgent need to expedite the process of implementing the Hydrogen Economy. A worldwide conversion from fossil fuels to hydrogen would eliminate many of the problems and their ramifications. The optimal endpoint for conversion to the Hydrogen Economy is the substitution of clean hydrogen for the present fossil fuels. The production of hydrogen from non-polluting sources (such as solar energy) is the ideal way [6]. Many environmental advantages can thrive within the Hydrogen Economy, and as such, it can be referred to as the Hydrogen Environmental Economy.

The utilization of solar quantum and thermal photons seems to be significant in the future work on hydrogen production. Solar hydrogen is not an energy, but a chemical energy carrier that enables worldwide loss-free storage and low-loss transportation of macro-economically relevant quantities of the secondary energies, heat or electricity. These can be generated from solar energy, albeit from solar irradiance, wind, hydropower, or ocean temperature gradients, or by using the two non-solar renewable energy sources, i.e. the motion of the tides and the heat of the Earths magma. Solar hydrogen makes it possible for solar energy to be traded on the worlds energy market. This market can thus be perpetuated beyond that point in time when the fluid hydrocarbons remaining in the Earths crust will no longer be available for energetic utilization. The status of research, development and demonstration of energetic solar hydrogen systems and their components were presented, including both scientific and technical aspects.

The amount of solar energy reaching the Earth is enough to supply mankind with many thousand times the energy it presently requires. This energy supply is, however, neither constantly available nor distributed equally over the surface of the globe. Indeed, the places where mankinds energy consumption is highest are not the places where the Sun’s irradiance is at a maximum. If the Sun’s daytime energy supply also has to be used at night, or its summer supply also in the winter, if the solar energy available at places with high insolation is also needed at places with low insolation and large energy demands, then it is physically impossible to meet these needs directly with the primary energy of solar irradiance.

Solar hydrogen is a clean energy carrier. Electrolytic hydrogen is made from water and becomes water again. Hydrogen obtained from solar energy (solar hydrogen) is ecologically responsible along its entire energy conversion chain. At only one link of the chain can a pollutant, nitrogen oxide, arise; and this occurs only if the hydrogen is not recombined with pure oxygen, but using air as an oxidant, such as in reciprocating piston engines or gas turbines on board automobiles or aircraft. At the high reaction temperatures which arise in such places, the oxygen and nitrogen in the air can combine to form nitrogen oxide.

Solar energy stored in hydrogen is available at any time and at any place on Earth, regardless of when or where the solar irradiance (or the hydropower, biomass, ocean energy or wind energy) was converted. The fundamental discrepancies in the times and places of solar energy supply and human energy demands can be overcome using hydrogen. Solar hydrogen makes solar energy as storable and transportable as oil and natural gas are by nature, but without the burden of their negative environmental impact. Solar hydrogen combines the advantages of hydrocarbons (storability and transportability) with the advantages of solar energy (ecological acceptability, renewability and low risk). Solar hydrogen has no need for the carbon atom, which makes the hydrocarbons almost infinitely storable at room temperatures, but is also the reason for their negative ecological impact. Solar hydrogen provides the link between the pre-industrial solar era, the first solar civilization, which only knew of stored solar energy in the forms of biomass and hydropower, and a post-fossil fuel era, the second solar civilization [7,8].

The worldwide photovoltaics market has grown rapidly in recent years, a growth that will continue in many areas, especially as grid-connected PV applications [9].

Hydrogen is a carbon-free fuel which oxidizes to water as a combustion product. The generated water becomes, together with renewable primary energy for splitting it, a source of clean and abundant energy in a carbon-free, natural cycle [10].

In the development of all new energy options, hydrogen necessarily will play an important role because of its ability to supplement any energy stream and apply to any load. Hydrogen will act as a solar storage medium and transform solar energy into a transportation fuel [11].

Recently, four solar hydrogen systems have been selected as showing sufficient promise for further research and development: (1) photovoltaic cells plus an electrolyzer, (2) photoelectrochemical cells with one or more semiconductor electrodes, (3) photobiological systems and (4) photodegradation systems [12].

2. Main approaches for hydrogen production

Much of the hydrogen produced in the world, and especially for the petrochemical industry, is obtained from natural gas, which is mostly made up of methane. The bulk production of hydrogen is through the catalyzed steam reformation of methane. However, the uncatalyzed partial oxidation of methane for appropriate optimization may be used to produce hydrogen at very attractive overall cost and energy efficiency. The combustion of rich mixtures of methane representing natural gas in air or oxygenated air involving the uncatalyzed partial oxidation of methane can be examined analytically. A detailed chemical kinetic scheme made up of 108 simultaneous reaction steps with 28 reactive species has been evaluated [13]. Water electrolysis is one of the most utilized industrial processes for hydrogen production today. The three major technologies currently under consideration for electrolytic hydrogen production are alkaline, polymer membrane and ceramic oxide electrolyte. Direct conversion of solar energy into hydrogen as a storable energy source can be achieved theoretically by photoelectrochemistry. The utilization of solar quantum and thermal

photons is important for technological progress, particularly for the high-temperature thermochemical and photochemical fields. Although the water splitting process to generate hydrogen and oxygen simultaneously has been reported by the utilization of light energy, it is not mature enough for pilot plant demonstrations. Much of the fundamental research remains to be done. Among the different approaches, photocatalysis has received much attention as a possible method for photochemical conversion and storage of solar energy. Photosynthetic bacteria represent a method with appreciable extent efficiency for hydrogen evolution using solar energy.

Certain hydrogen production processes have reached maturity for commercial exploitation: (a) steam reforming of natural gas; (b) catalytic decomposition of natural gas; (c) partial oxidation of heavy oils; (d) coal gasification and (e) steam-iron coal gasification. Other processes, such as thermochemical, photochemical, photoelectro-chemical and photobiological processes are being explored or already at the research and development stage. The main processes for hydrogen production and their status of development are summarized in Table 1.

2.1. Electrochemical processes

Water electrolysis is one of the most important industrial processes for hydrogen production today, and is expected to become even more important in the future. The three major technologies currently under consideration for electrolytic hydrogen production are classified as alkaline, polymer membrane and ceramic oxide electrolyte. Development of solid electrolytes for water electrolysis at intermediate temperatures is important [15].

Critical to the electrochemical situation is the work of Kainthla et al. who carried out calculations that gave rise to the theory of how two photovoltaics could be coupled together [16]. It was shown that the relation of their energy gap to the flatband potential was critical. The substances which the theory indicates are suitable

Table 1
Summary of main hydrogen production processes [14]

Production process	Status
Steam reforming of natural gas	Mature
Catalytic decomposition of natural gas	Mature
Partial oxidation of heavy oil	Mature
Coal gasification	R and D—Mature
Steam-iron coal gasification	R and D
Water electrolysis	Mature
Thermochemical cycles (pure)	R and D
Thermochemical cycles (hybrid)	R and D
Photochemical processes	Early R and D
Photoelectrochemical processes	Early R and D
Photobiological processes	Early R and D

(non-oxides) would form oxides upon the evolution of oxygen, so that it was necessary to coat them with a non-permeable coating.

A principal focus of modern research in hydrogen production by electrolysis is to discover electrode materials that exhibit good electrochemical stability and show interesting activity for the typical electrochemical reactions. It is also desirable that these materials be inexpensive, abundantly available, easy to manipulate and non-polluting. Such a class of materials is represented by metal silicides [17].

The current-voltage behavior of hydrogen evolving Raney-nickel electrodes has been extensively explored [18]. Raney-nickel cathodes prepared by different methods are increasingly applied in the most important electrochemical technologies. The effectiveness in enhancing the catalytic activity of nickel electrodes by employing three types of particulate materials, namely Raney-nickel, aluminium and alumina powders during the cathodic codeposition of nickel has been researched [19].

The catalytic activity of Nickel-iron alloy cathodes prepared by electroplating is reported in Ref. [20].

Stationary polarisation curves were obtained for a porous nickel electrode under varying temperatures and anode gas compositions. Slopes were studied at low over-potentials [21].

Hydrogen evolution reaction mechanism on electrodeposited Ni–S coatings of low sulfur content was initially studied in alkaline solutions through steady-state polarization measurements. Tafel plots have been analyzed at several temperatures and varying pH values. The results suggested a mechanism involving fast electron transfer followed by a slow electrochemical desorption step [22]. The hydrogen evolution in the basic medium of iron or nickel electrodeposited with heteropolyacids has been investigated [23].

A comparative study of the behaviour of various Ni-doped and undoped Mg-MgH_2 materials to be utilized for reversible (thermochemical) high temperature heat or hydrogen storage has for the first time been conducted over a broad range of hydrogenation/dehydrogenation(cycling) conditions [24].

Solid polymer electrolyte technology, i.e. proton exchange membrane technology in which the two electrodes are coated or pressed onto a membrane used as the electrolyte, is the most promising candidate for low temperature fuel cells [25].

In order to create a CO_2 neutral, regenerative energy system based on methanol, a new coupled process has been proposed through the production of hydrogen by water electrolysis and CO_2 from the atmosphere [26].

The electrochemical reduction of CO_2 with a Cu electrode in LiOH/methanol-based electrolyte was investigated [27].

The decomposition of water into hydrogen and oxygen under sunlight has been studied. The rate of produced hydrogen has been increased by the aid of solar cell and double liquid electrolysis [28].

2.2. Thermochemical processes

More than 200 thermochemical cycles have been reported, but the technical status of many of them is at the experimental or bench-scale stage. The main reason for

this is the technical problems to be solved before commercialization, such as the separation of products and the circulating agent and equipment development for industrialization. In addition, thermochemical reactions may cause pollution problems if the process is not completely closed.

A search program which uses only the free energies of formation has been developed to find new thermochemical cycles for the production of hydrogen from water. Some representative closed cycles mainly composed of copper compounds with three-step reactions have been presented. The KIER-3 cycle using copper oxide and copper sulfate seems to be the most practical one among them [29]. Thermochemical water splitting cycles through direct HI decomposition from H_2O–HI–I_2 solutions and the results for different concentrations and temperatures up to 220°C have been reported [30]. A number of potential thermochemical water splitting processes have been evaluated quantitatively by computer model evaluations.

The redox systems studied, which could achieve decomposition of water in two steps by condensed redox phases, were the oxide systems $CoO(Co_3O_4$,MnO Mn_3O_4,FeOFe_3O_4,$NbO_2Nb_2O_5)$ and the halide systems $FeX_2Fe_3O_4$, where X = F, Cl, Br or I. The results from the calculations have been utilized to outline the conditions for hydrogen production and possible deoxidization and reformation subprocesses [31].

Ceramic-based support materials are of interest for hydrogen production through the UT-3 thermochemical water-decomposition cycle [32–34]. The UT-3 thermochemical water-decomposition cycle requires Fe reactant pellets with high activity and long life. Properties of Fe reactant pellets using ZrO_2–Y_2O_3,$ZrSiO_2$+ZrO_2 as support materials have been evaluated [35].

Recently, new data on yields of hydrogen iodide from oxidation of dehydrated disulfide monosulfate 4-hydrate, admixed with a cerium dioxide substrate, were reported. Some of these data have been used for evaluation or modification of the sulfur dioxide-iodine thermochemical cycle for hydrogen production [36].

A new two-step thermochemical cycle for hydrogen production has been suggested and the main reactants, Cr_2O_3 and MOH (M = K, Na, Ba or Mg), have been tested [37].

The ability of some zeolite to generate hydrogen from hot steam after their vacuum activation as well as the influence of parameters (pressure and temperature) on water dissociation were already reported [38–47].

A thermocatalytic process for hydrogen generation has been developed using water in the presence of zeolite catalysts impregnated with non-noble metals of variable valences and activated in vacuum [48]. For optimizing the technological flow, continuous decomposition of water in reaction-regeneration catalyst cycles in moderate vacuum at temperatures up to 500°C has been achieved [49]. Two methods for the activation of zeolites have been established: (1) vacuum outgasing at temperatures ranging between 300 and 500°C, and (2) activation of zeolites with UV and UV-IR radiation. An electronic microbalance (10^{-6} g) has been used for measurements of weight variations of zeolites during their activation. The activation–deactivation curves have been generated. An experimental device has been built for the catalytic

decomposition of water over zeolites with the capability of measuring mass variation of zeolites during irradiation [50].

Hydrogen evolved in thermal decomposition over zeolites was highest value when the HCl aqueous solution was added [51].

A reactor has been built to study the hydrolysis of $FeCl_2$ for the hydrogen generation step in the thermochemical cycles from the Fe-Cl family. Equipment for high temperature kinetic studies on gas–solid heterogeneous reactions have been described. The preliminary test results and some problems generated by the use of anhydrous $FeCl_2$ as solid phase and corrosive character of the gaseous phase, due to the presence of HCl have been presented [52]. The criteria for the selection of the thermochemical cycles used to establish the maximum efficiency for multi-step water splitting have been analyzed. A model for performing the selection of thermochemical water splitting cycles has been presented. The steps for having a negative contribution to the overall thermal efficiency have been identified [53].

On a basis of some computer calculations a measure of catalytic power of the metals and alloys was defined and the series of metals and alloys was ordered according to their catalytic power. It was found that the highest catalytic power with respect to the hydrogen dissociation process is exhibited by NiCu alloys [54].

2.3. Photochemical processes

Considerable attention has been given to the process of splitting water into hydrogen and oxygen with the use of sunlight, because it could result in a low-cost method of producing hydrogen [55]. As is well known, the spatial distribution of solar radiation may be strongly non-uniform. Indeed, the amount of solar radiation at ground level depends on the latitude and some other factors, such as the altitude and the atmospheric conditions. Consequently, studies concerning the meteoro-climatological features of a given site must be considered before designing a solar installation there. In order to estimate the availability of solar global radiation, the Angstrom–Page formula can be used. The relationship predicts the value of relative sunshine (the ratio between the hours of bright sunshine and the daily light hours) [56].

One of the possibilities of hydrogen production by solar energy is the direct photochemical reduction of water. A sensitizer is excited by visible light and can thereafter affect redox reactions, yielding electrons for the water reduction. One of the benefits of this system is that several sensitizers with different absorption characteristics can be used simultaneously, leading to higher quantum yields per unit area. The ground and excited states of sensitizers differ significantly in the redox potentials. Usually, the more electronegatively excited sensitizers deliver the needed electrons for the water reduction.

For the photochemical reduction of water, a catalyst is usually needed, and in most cases, a heterogeneous noble metal catalyst is used. These metals are generally present as small particles, and to impede precipitation a protective agent (usually a polymer) is added, which reduces the catalytic activity. With such catalysts, it is difficult to obtain reproducible results, since diminutive variations in the synthesis

may result in considerable deviations in the activity of the catalyst. The aging of the catalysts is also important.

Systems using colloidal noble metals as catalysts need a separate electron relay compound. One of the main problems with such electron relay compounds is the hydrogenation of their double bonds, and that their reduced forms (radicals) are often very reactive towards oxygen.

A better choice would be a homogeneous catalyst with high catalytic activity, and hence no precipitation problem. Further, with a homogeneous catalyst, a better distribution around the sensitizer molecules can be obtained. Various enzymes have been tested as water reduction catalysts, but none of them has worked efficiently. A homogeneous water soluble Wilkinsons catalyst has been investigated by Oishi, and showed excellent catalytic activity for water reduction. This substance combines the features of an electron relay compound and a catalyst that exists in different redox states [57].

It has been confirmed that the bifunctional redox catalyst $PtBi_2O_3RuO_2$ mediates photocleavage of water in the presence of MV^2 on irradiation with visible light of > 410 nm in the presence of $Ru(bpy)^{2+}{}_3$ with a light of > 450 nm [58].

A common problem in reactor design is the determination of the extensive reaction rate as a function of the intensive rate, the flow model and the geometry of the system. For a photoreactor, the issue is complicated by the fact that the rate depends on the distribution of radiation on it. The determination of this light distribution is very complex for the heterogeneous catalytic systems. This problem has been undertaken for tubular reactors with photocatalytic membranes supported on spheres or concentric cylinders. Computer simulation programs based on the Monte Carlo method have been developed for the case. The influence of several variables, such as the absorbency of the catalyst and the support, the refraction indexes and the diameter of the spheres, has been studied. The radiation absorption efficiencies of different systems of supporting the photocatalytic membranes have been compared, and design equations based on simulation results have been proposed [59].

The photophysics and photochemistry of the adsorbed layer remained one of the most unexplored fields in photochemistry for a long time, when compared with studies in homogeneous systems. Recently, studies of the photophysics and photochemistry of molecules adsorbed on inert adsorbents, such as SiO_2 and zeolites, have received a great deal of attention from the standpoint of photochemical processes on solid surfaces, providing a new research field, namely heterogeneous photochemistry. In addition to these, however, more recent studies of surface photochemistry have been given a great deal of attention due to their potential for yielding a promising number of useful applications including the control of photochemical reaction paths and conversion of light energy to useful chemical energy.

In connection with the problem of adsorption and catalysis, a number of studies were carried out in the field of photocatalysis, which were initially concerned with the effect of irradiation of the catalysts in their fundamental adsorption bands on their catalytic activities and selectivities for catalytic reactions. In this case, the reactant molecules usually show no absorption in the absorption regions of the catalyst. Instead of activating a solid catalyst by irradiation, however, it seems possible that

a reactant or an intermediate complex formed on the surfaces is activated by irradiation, which results in acceleration of the reaction or the occurrence of a new reaction. Recently, this field has been expanding rapidly in connection with light energy, especially in the conversion of solar energy to chemical energy using solid catalysts such as TiO_2 [60].

2.4. Photocatalytical processes

Solar utilization via chemical storage can be achieved by photocatalytic and/or photoelectrochemical activation of light sensitive semiconductor surfaces. The absorption of photons corresponding to the fundamental absorption band of the catalyst leads to the formation of electron-hole pairs, some of which undergo radiative decay as photoluminescence. Therefore the studies of photoluminescence (PL) in the presence of reactant molecules are expected to be useful not only in understanding the surface structure and the excited states of the catalysts, but also as a probe for surface processes leading to the photochemical production of electrons and holes. However, although TiO_2 catalysts are known to exhibit high activity for decomposition of H_2O, few PL studies have been carried out in connection with photocatalysis and/or photoconductance. The addition of unsaturated hydrocarbons onto the TiO_2 catalyst causes an increase in intensity of PL of the catalyst as a radiative surface process from photoformed electrons and holes. The extent of the PL enhancement strongly depends on the ionization potential of the added compounds, i.e., the lower the ionization potential of the added compound, the larger the PL intensity. A parallel relationship between the enhancement of the TiO_2 by the addition of the unsaturated hydrocarbons and the rate of photocatalytic hydrogenation of these compounds with H_2O on the TiO_2 catalysts, suggests that these surface processes are closely associated on binding of the added molecules to the TiO_2 surface [61]. The influence of altervalent cation doping of TiO_2 on its performance as a photocatalyst in water cleavage has been investigated. It has been shown that under illumination in the near-UV region, platinized anatase exhibits hydrogen production rates which are significantly higher than those of the rutile form [62].

Superoxide (O^{2-}) has been shown to be readily generated in aqueous solutions with vacuum-UV lamps of simple design. A mechanism has been proposed and shown to account for the results by comparison to computer calculations [63].

Photocatalytic decomposition of water into hydrogen and oxygen using semiconductors loaded with various metals have been widely studied [64]. An addition of Na_2CO_3 played an excellent role for the stoichiometric photodecomposition of liquid water over TiO_2 and $SrTiO_3$ loaded with various metals such as Pt, RuO_2 and NiO [65].

Water photolysis has been studied in liquid phase using neutral aqueous suspensions of RuO_xPtTiO_2 particles and UV light. The role played by oxygen in catalyst activity was marked [66].

An inexpensive method of forming monolithic porous titania glass has been reported, as well as some properties that make it uniquely suited to photocatalytic applications, such as its inexpensive fabrication, its high surface area, and its spon-

taneous photoformation of hydrogen from water without the need for precious metals [67–69].

2.5. Photoelectrochemical processes

Research area of photoelectrochemical cells has grown extensively over recent years. The temperature dependency of the resistance and photoelectrochemical properties of the superconducting samples of Y–Ba–Cu–O and Bi–Sr–Ca–Cu–O doped with different ligands have been investigated [70]. Silicon and gallium photoelectrodes have been investigated for solar hydrogen production [71,72].

Very interesting aspects of solar hydrogen production from hydrogen sulfide using semiconductor powders have recently been reported [73]. Haematite and magnetite-based coating obtained by thermal oxidation of conversion coatings could be used as photoanodes [74]. Photoelectrochemical semiconductor septum (CdSeTi and TiO_2Ti) solar cells in relation to hydrogen production have been found [75]. A major problem of photoelectrodes for hydrogen production is the photo-corrosion of the photoanode surface [76].

In order to develop a clean burning fuel from renewable sources, methanol is a practical option as a possibility for solar hydrogen storage. The electrochemical reduction of CO_2 to CH_3OH is thermodynamically more convenient than hydrogen generation, but this process is kinetically inhibited. The development of new electrocatalysts shows that the overvoltage of this reaction could be minimized [77].

Direct conversion of solar energy into hydrogen as a storable energy carrier can in principle be achieved by photoelectrochemical means. However, despite high conversion efficiencies obtained in wet solar cells for the conversion into electrical energy using reversible redox systems in the electrolyte, the direct splitting of water using visible light has not been achieved yet. Recent progress in understanding and possible ways to overcome the underlying basic problems have been reported. The main task to solve is the modification of the semiconductorelectrolyte interface [78]. In principle more detailed investigations confirm the high quality of the semiconductor electrolyte interface which is necessary to obtain high conversion efficiencies. High efficiencies have been obtained in laboratory solar cells [79].

2.6. Photobiological processes

Photosynthetic bacteria represent a futuristic approach with appreciable extent of light-conversion efficiency [80]. Whey, a by-product of the milk processing industry, has also been used as the efficient substrate for hydrogen production by photosynthetic bacteria [81]. The sustained hydrogen production by immobilized cells by a strain of Rhodopseudomonas at the expense of potato starch [82] and the insolation of high temperature strains showing significant hydrogen production even up to 45°C have been reported [83]. Four strains of Rhodopseudomonas sp. evolved hydrogen at the expense of potato starch, sugarcane juice and whey in the presence of light (2klx)—anaerobic condition (argon CO_2, 955, vv). Among the three substrates, sugarcane juice supported the maximum level of hydrogen production followed by

potato starch and whey at the rates of 45, 30 and 25 ml H_2 h^{-1} mg^{-1} bacterial cell dry wt, respectively [84].

Hydrogen production is catalyzed by nitrogenase or by the reversible hydrogenase. The functioning of nitrogenase, as well as hydrogenase, is linked to cyanobacteria with the utilization of the products of photosynthetic reactions that generate reductants from water. Thus, it is possible to design bioreactors in which solar energy could be used to produce hydrogen from water with cyanobacteria as biocatalysts [85]. It is of interest to investigate other conditions for hydrogen production that are cheaper and more convenient for practical bioreactors than hydrogen formation under an argon atmosphere. Molecular hydrogen production by nitrogen-fixing cyanobacteria Anaebaena variabilis and Nostocmuscorum has been induced by a partial vacuum. A laboratory scale hollow fiber photobioreactor has been assembled for continuous production of hydrogen by immobilized cyanobacterium A.variabilis under a partial vacuum. The hollow fibers were composed of semi-permeable polymeric membranes [86]. The bioreactors were designed to allow free movement of small molecular weight nutrients, gases and waste products between the outer surface of the fibers and the inner space (lumen) of the fibers. The cells, due to their large size, are situated on the outer surface of the fibers. All these features are very helpful for the separation and concentration of the products from cell cultures. Another important advantage of the use of hollow fibers for bioreactors is the large surface-to-volume ratio, which allows the design of compact systems. In addition, the photosynthetic activity and hydrogen production are stabilized by immobilization of the cells on solid surfaces. Photoproduction of hydrogen by the nitrogen-fixing cyanobacteria A. variabilis and N. muscorum has been induced by a partial vacuum. A laboratory scale photobioreactor has been designed so that the cyanobacterial growth medium passes from the outside of the fibers into the inner lumen space. Photoproduction of hydrogen at rates 0.002–0.2 ml H_2 mg^{-1} dry wt h^{-1} of cyanobacterial biomass have been observed. The photobioreactors were run for five months with continuous production of hydrogen [87]. Hydrogen production using micro-organisms in hollow fiber bioreactors has been investigated [88].

The generation of electricity from biomass has been the subject of interesting modern projects [89].

While today carbon based chemical energy and hydrogen to a large extent produced from fossil, regenerative biomass will be the source in a hydrogen economy) [90].

3. Technologies of hydrogen storage and transport

Most liquid or gaseous hydrogen/carbon materials can and do serve as fuels for road vehicles. The main groups are:

- other fossil fuels, such as natural gas, LNG (liquefied natural gas) or LPG (liquefied petroleum or propane gas)
- renewables and waste such as biodiesel, biogas, landfill gas and the alcohols.

- derived fuels such as methanol, hydrogen and electricity [91].

There are four technologies available today to store hydrogen aboard vehicles [92]:

- liquefied hydrogen—used by NASA—and considered for airliners.
- metal hydrides—used for example by Mazda and by Daimler-Benz in passenger cars.
- compressed hydrogen gas—used on urban transport bus built by Ballard.
- carbon sorption—yet to be used on vehicles.

In recent years, many technologies have been developed. Among them, the following were reported:

- preparation and study on electrochemical characteristics of Mg2Ni system hydrogen storage alloy [93].
- design of a two-stage metal hydride system for the use in cascading sorption systems [94].
- a large experimental apparatus for measuring thermal conductance of LH2 tank [95].
- new carbon variants: graphitic nanofibres and nanotubes as hydrogen storage materials [96].
- the effect of the La/Ce Ratio on the electrochemical performance of hydrogen storage alloys [97].
- adsorptive storage of hydrogen on carbon adsorbents and its engineering prospect [98].
- liquid-film type catalytic decalin dehydrogeno-aromatization for mobile storage of hydrogen [99].
- hydrogen densification in metal hydride [100].
- improvement on the cycle life of Mg-based hydrogen storage alloy prepared by mechanical alloying [101].
- hydrogen supply system of small proton exchange membrane fuel cell power source [102].
- nonstoichiometric laves phase alloys as efficient hydrogen storage media [103].
- preparation and hydrogen storage process of nanocrystalline Mg_2Ni prepared by mechanical alloying [104].
- preparation of composite materials of carbon nanotubes at room temperature [105].
- nanocrystalline Zr-based AB2 Alloys for hydrogen storage [106].

4. Economics

An adequate comparison of hydrogen costs of the actual hydrocarbon energy has to take into account the external costs i.e. costs for pollution abatement/prevention and climate effects of fossil fuel burning. If the costs for pollution abatement orig-

inating from fossil energy use are available only very approximately the cost of the negative drawbacks on climate changes are clearly imponderable i.e. impossible to evaluate numerically.

The hydrogen cost of 15 $cents_{ECU}$/kWh can be compared with the cost of taxed gasoline prices in Europe (average of the 12 EC countries, August 1990) of 8.5 $cents_{ECU}$ /kwh which are made up of 3 $cents_{ECU}$/kwh for the crude oil itself, its transportation, refinement, manipulation and distribution and of 5.5 $cents_{ECU}$/kwh for taxes.

With the internalization of external costs, hydrogen energy would thus be about 2.9 times higher than hydrocarbon energy costs, not taking into account the imponderable costs of climate effects. In the absence of carbon atoms, hydrogen fuel would not be subjected to mineral oil taxes [107].

The first hydrogen hybrid-electric vehicles introduced with home electrolysis will have fuel costs competitive with battery-powered vehicles, in large part because of the capital investment for electrolysers [108].

Technical and economic feasibility studies have been performed on several renewables-based hydrogen production processes. Highly detailed analyses have been conducted on processes to produce hydrogen from biomass; these processes are indirectly heated gasification followed by steam reforming of the syngas, and pyrolysis followed by steam reforming of the pyrolysis oil. Because biomass pyrolysis oil is similar to crude oil in that many chemicals and fuels can be derived from it, the impact of coproduct options on the economic of producing hydrogen from pyrolysis-based technologies was also studied. Economic assessments of solar and biologically-based hydrogen production processes have focused on the steps that need to be taken to improve the competitive position of these technologies. Within the United States Hydrogen Program, a number of technologies are used to evaluate and compare hydrogen technologies. Technical and economic analyses can be conducted, and serve to determine process economic potential. Analyses have been conducted on the process being studied at the National Renewable Energy Laboraratory to produce hydrogen from renewable resources. These processes include gasification and pyrolysis of biomass followed by steam reforming, photoelectrolysis, hydrogen production by green alga, and water-gas shift by immobilized bacteria. Additionally, a novel storage medium and a hydrogen leak detector have been investigated. Results have determined at which points these various research tasks will become feasible in the near-, mid-, and long term. Further, the outcome of each analysis has been used to plan future research [109].

The economic studies were structured to duplicate typical local, regional and remote local conditions. The following feedstock and energy costs were used in the analysis:

1. Natural gas—$3.79/GJ ($4/MMBTU) at a small reformer, $2.85/GJ ($3/MMBTU) at a regional medium scale unit, and $1.90/GJ ($2/MMBTU) at remote large scale units.
2. Electric power—$0.07/KWH for a home electrolysis unit, $0.05/KWH for con-

Table 2
Cost analyses for hydrogen infrastructure to supply fuel cell automobiles

	Size tonnes/day	Investment $-thousand	Cost $/kg
Scenario #1: Remote reformer + liquefier	27	$63 000	$3.35
	270	$259 000	$2.35
Scenario #2: Local reformer + pipeline	27	$82 000	$2.91
	270	$67 000	$2.47
Scenario #3: On=site natural gas reformer	2.7	$96 000	$3.57
Scenario #4: Partial oxidation of oil	2.7	$12 500	$3.96
Scenario #5: Electrolysis of water	3 kg/day	$13.5–$23.1	$6.97
Scenario #6: Methanol reformation	2.7	$6800	$3.76

tinuous usage at on-site, regional and remote plants, and $0.03/KWH at all locations during “off-peak” periods.
3. Methanol at a market price of $0.18/liter.
4. Heavy oil at $0.09/liter.

As evident from Table 2, hydrogen would be priced at between $2.35 to $7 per kilogram depending upon the size, and location of the market. Hydrogen can be liquefied at a very low temperature (20°K) and stored at low pressure in super insulated tanks [110].

Table 3 shows the effective costs of fuels which include the environmental damage caused by these fuels, for ICE vehicles for a range of 300 miles [111].

The cost of electrolytic hydrogen is comparable to synthetic hydrocarbon fuels,

Table 3
Effective costs of fuels for 300 mile range ice vehicles for year 2000

Fuel	Cost range (1996 $/km)		Median cost (1996 $/km)
	Lower cost	Higher cost	
Wind-H_2	0.0848	0.1251	0.1049
PV-H_2	0.0947	0.1710	0.1329
Hydro-H_2	0.0487	0.0869	0.0678
Biomass-H_2	0.0410	0.0565	0.0487
NG-H_2	0.0559	0.0786	0.0673
Ethanol	0.0616	0.0763	0.0689
Methanol	0.0487	0.0545	0.0516
CNG	0.0386	N/A	0.0386
LPG	0.0464	0.0484	0.0474
Gasoline	0.0594	N/A	0.0594

and about three times as expensive as hydrogen from fossil fuel sources [112] (Fig. 1).

5. Environmental benefits

The combustion of hydrogen does not produce CO_2, CO, SO_2, VOC and particles, but entails emission of vapour and NOx.

Water vapour emissions from airplanes may be harmful since they generate—depending on the cruising altitude and latitude—ice clouds with ensuing greenhouse effects and ozone depletion, the problem is of great importance and actually under investigation.

The formation of NOx is a function of flame temperature and duration. Considering the wide flammability range of hydrogen its combustion can be influenced by the design of the engine so that the NOx emission can be reduced.

The worldwide water evaporation from consumption the oceans and rivers is ~5.10^{14} m^3 per year. If mankind's today's total energy consumption of sustained 11 TW would be effectuated by hydrogen, the ensuing yearly water evaporation would be ~$2.5.10^{10}$ m^3 i.e. about 1/20 000 of the natural evaporation. Once hydrogen will be massively used, local considerations are obligatory like it is the case for today's cooling towers [107].

Recent research regarding air pollution effects on human health describes serious lung damage sustained from fossil fuel combustion. Substituting hydrogen for fossil fuel will result in improved physical health [113].

Is a major option to slow down the rate of atmospheric CO_2 emissions or level out the CO_2 concentration in the atmosphere. A unique system has been devised which offers a method of actually reducing the CO_2 concentration in the atmosphere while still generating energy from fossil fuel. The only economically and technically

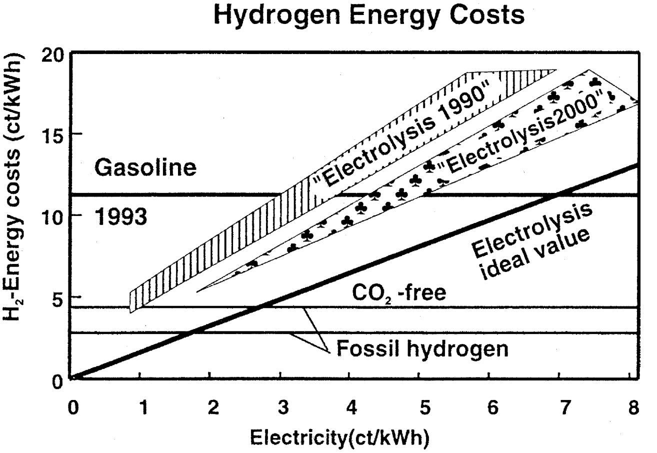

Fig. 1. Comparison of hydrogen costs.

reasonable method for removal of CO_2 from atmosphere is by the process of solar photosynthesis which extracts carbon from atmospheric CO_2 by formation of biomass, e.g., lignocellulose. The biomass is then thermochemically converted by the HYDROCARB technology with fossil fuel, gas oil or coal to produce carbon black and methanol. The carbon is returned to the earth, for longterm storage, while the methanol is used as fuel. In this manner, methane gas and oil coprocessed with biomass results in a net removal of CO_2 from the atmosphere of about 78 lb CO_2 per milion Btu of methanol generated energy. There is also large energy enhancement in utilizing gas and oil for producing methanol compared to conventional methanol process using these fuels. Coprocessing with bituminous coal results in no net CO_2 emmitted or removed per unit of methanol energy generated [114].

In Table 4, CO_2 generation from various fuels is presented.

There is a new important development in automative technology in recent years which is aimed towards more efficient and less polluting vehicles.

The analysis of full cycles shows that the fuel cell drive for city buses offers significant environmental improvements compared to diesel internal combustion engines. This refers to emissions of greenhouse gases as well as to local emissions of trace gases. The main improvement with regard to the global warming problem can nonetheless only be achieved if renewable fuels are introduced [115].

A major advantage of fuel cell vehicles (and all fuel cells) is that they represent an inherently clean, efficient and quiet technology and can optimize use of fuels from environmentally begin energy sources and feed stocks such as solar, wind, geothermal and biomass. One must emphasize these attributes to the maximum extent possible because there is increasing competition from conventional technologies [116].

Table 4
CO_2 generation from various fuels

Fuel type	Chemical formula	Value BTU/lb	CO generated lbs CO_2/lb fuel	CO generated lbs CO_2/MMBTU	Energy generated Kw H(E)/lbCO_2
Natural					
Bituminous coal	CH0.8O0.1	12 700	2.59	215	0.56
Fuel oil and gasoline	(CH2)N	19 600	3.14	160	0.70
Biomass (wood)	(CH2O)N	8000	1.47	180	0.62
Natural gas	CH4	24 000	2.75	110	1.01
Synthetic					
SNG from coal gas	CH4	24 000	7.90	330	0.34
Liquid HC from coal liq.	(CH2)N	20 000	6.30	310	0.36
Hydrogen from natural gas	H2	61 000	7.00	110	1.01
Hydrogen from coal liq.	H2	61 000	16.50	270	0.41
Hydrogen from non-fossil energy (Hydro, solar, nuclear)	H2	61 000	0	0	–

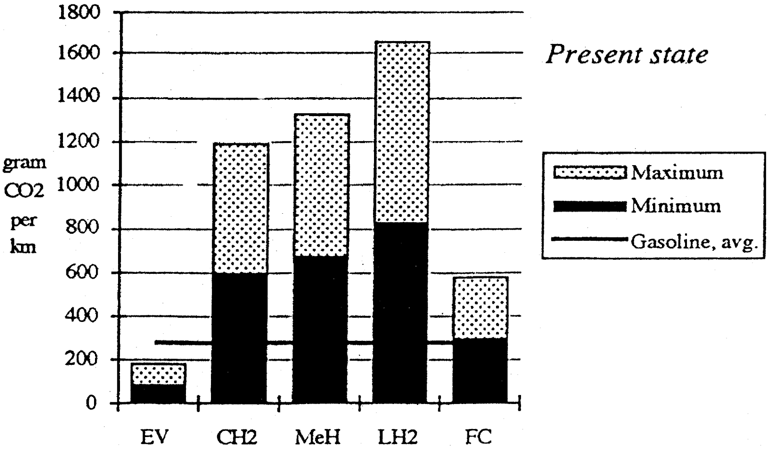

Fig. 2. Specific CO_2-emissions of electric and hydrogen vehicles (1996).

The calculated CO_{2-} emissions for an average car with electrical propulsion as well as with different hydrogen technologies are presented [117]. Fig. 2 shows the present situation with respect to technological level and power supply system, whereas Fig. 3 shows the projected situation in the year 2030. The hydrogen technologies include three different hydrogen technologies based on ICE drive trains—liquid hydrogen (LH2), compressed gas storage (CH2) and metal hydride storage (MeH)—and on based on fuel cells (FC).

In the case where utilization of solar energy and hydrogen is introduced in the energy market, energy consumption continues to increase, although at a lower rate than between 1950 and 1990 (Fig. 4).

Hydrogen introduction dramatically affects carbon dioxide in the atmosphere, which reaches the maximum before 2050 at 520 ppm (Fig. 5).

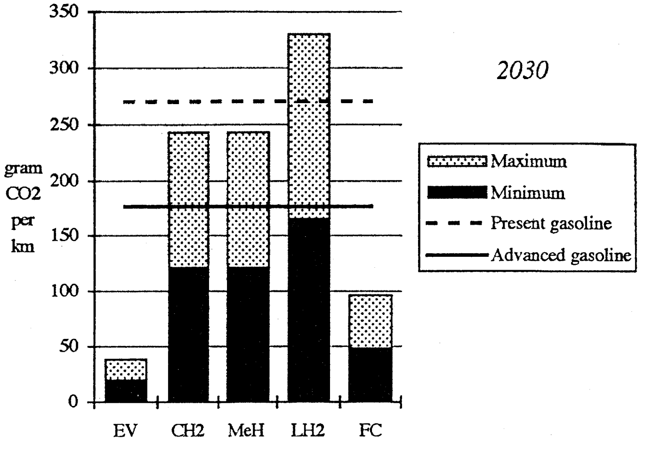

Fig. 3. Specific CO_2-emissions of electric and hydrogen vehicles (2030).

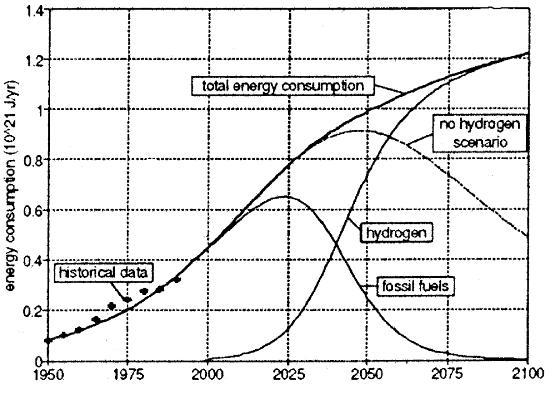

Fig. 4. Energy consumption (base case scenario).

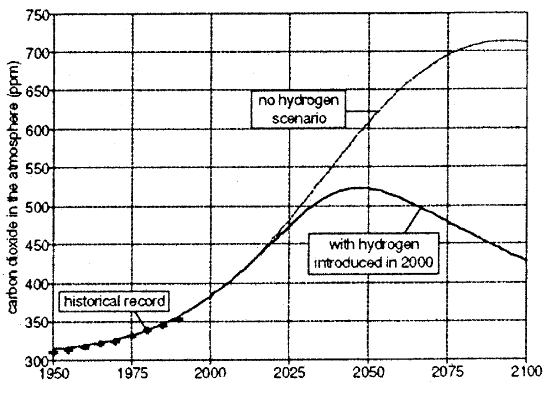

Fig. 5. Carbon dioxide in the atmosphere (base case scenario).

Figs. 6 and 7 show what would happen if transition to the solar hydrogen system is delayed 25 years. Energy consumption and economic activity would be higher than in “no hydrogen” scenario, but much lower than the case when hydrogen is introduced in the year 2000. Carbon dioxide would continue to increase until approximately 2070 reaching 620 ppm. If transition starts at 2050 there would be almost no positive effects. This suggests that an early transition to the solar hydrogen energy system would benefit the economy and the environment in the long run [118].

We need to use a fuel that is clean and efficient that does not cause cancer, smog, or dirt. Hydrogen is such a fuel. It makes sense to use the forms of energy that are abundant, clean and renewable. The sun and hydrogen have been coupled since the beginning of time and will be producing energy together for a span of time beyond anyone’s imagination. For a healthier life it makes sense for us to use solar-hydrogen [119, p. 54].

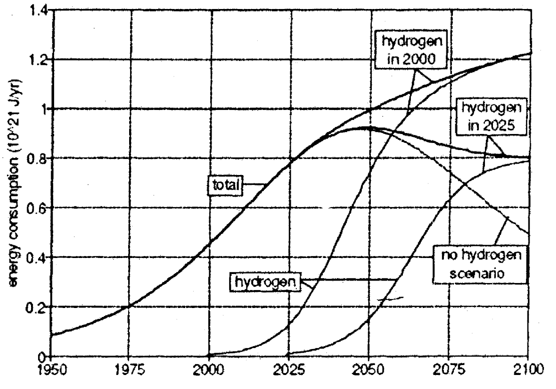

Fig. 6. Energy consumption (initiation of hydrogen energy system is delayed 25 years).

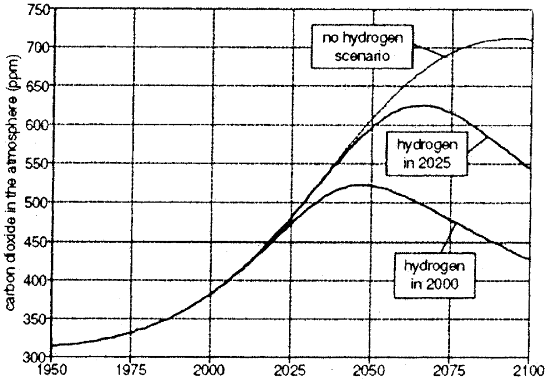

Fig. 7. Atmospheric carbon dioxide (initiation of the solar hydrogen energy system is delayed 25 years).

6. Hydrogen energy status in the world

This chapter will provide an overview of the hydrogen energy status around the world at the end of the 20 century. Different countries are presented in connection with their implications in hydrogen energy production and utilization.

Significant interest in the development of hydrogen vehicle technology has yet to *emerge* in the *USA*.

An important opportunity exists, however, for hydrogen to become established as the succesor to a natural gas-based transportation strategy when the supply of natural gas eventually dwindles and the cost of producing hydrogen from renewable energy resources declines [120].

Hydrogen research is developed in *Hawaii*. There is Hawaii's natural Energy Institute's Hydrogen from renewable resources research program [121].

The concept of a hydrogen-based, clean, renewable energy system, conceived by the Joint Research Centre *Ispra* of the Commission of the European Communities,

is investigated by European and *Canarian* Industries, coordinated by JRC-Ispra of the Commission of the European Communities and the Government of *Quebec*.

The 100 MW pilot project is to demonstrate the provision of clean and renewable primary energy in the form of already available hydroelectricity from Quebec converted via electrolysis into hydrogen and shipped to Europe, where it is stored and used in different ways: electricity/heat cogeneration, vehicle and aviation propulsion, steel fabrication and hydrogen enrichment of natural gas for use in industry and households [122].

A status report on the demonstration phases of the Euro-Quebec hydro-hydrogen pilot project was reported [123].

The relatively high costs of conventional alternatives make *Northen Canada* a logical niche market where hydrogen can be competitive on a purely performance and economic basis [124]

The largest hydropower plant in *Brazil and South America* is Itaipu and it pertains Brazil and *Paraguai*. Itaipu has a lot of secondary energy disposal because of its size, the one is lost as energy spilled no turbined in the reservoir. From this energy electrolytical hydrogen is produced. The hydrogen is produced as a gas after can be storaged as a liquid, pressurized gas, metal hydride, and transported for other places in the same country or to other country for use as energy [125].

A study of the costs for the different stages in the process of generating, storing, and transportation liquid hydrogen (LH_2) at low temperature, obtained from wind power in the *Argentine Patagonia* was reported [126].

A feasibility study about developing PEM fuel cell bus technology was developed in *China* [127].

The study for the WE-NET Project in Japan examined the potential for reduction in nitrogen oxide emission with hydrogen fuel in the *Tokyo* metropolitan area where sufficient data exit on trends in population, vehicle registrations, traffic activity, and exhaust emissions [128].

Different technologies of hydrogen production suitable for Libya have been reviewed and the possibility of harnessing wind energy in *Libya* in order to produce hydrogen using conventional water electrolysis was considered [129].

Solar hydrogen is produced by photovoltaic near Cairo, *Egypt* [130].

In *Russia* there is progress in fuel cell development and possible market. Among the main fields of application there are gas and oil industry, renewable energy systems for decentralised energy in remote regions, emergency power supply (including electric power stations) and certainly vehicles [131].

In *Iceland*, there are new concepts concerning the production of hydrogen as a fuel, using geothermal energy [132].

Europe has gained a leading position with regard to use of hydrogen technologies. In recent years, European industry has realized several hydrogen vehicle prototypes and demonstration vehicles equiped with internal combustion engines (ICE) and proton exchange membrane fuel cell electric drives (PEMFC) combined with onboard storage systems using compressed gaseous hydrogen (CGH_2) or cryogenic liquid hydrogen (LH_2). These new developments include passenger vehicle projects by BMW(LH_2), Renault (LH_2) and ZEVCO (CGH_2), van type vehicles by Daimler-

Benz (CGH_2), Hamburg Hydrogen Association (CGH2), PSA (CGH_2) and ZEVCO(CGH_2) as well as city buses by Ansaldo (LH_2), Daimler-Benz (CGH2), Hydrogen Systems (LH_2), MAN (LH_2 and CGH_2), Neoplan(CGH_2). Recently, numerous activities, including retrofit as well as standard production ICE cars, buses and trucks, have also been observed in the field of natural gas (CNG and LNG) which could pave the way to hydrogen [133].

In the *Canary Islands* the objective of project CanarHy is to design a self-sufficient system obtaining its primary energy from wind turbines and capable of generating electricity and producing heat and drinking water [134].

A hydrogen energy system is being considered for energy supply of the *Dalmatian Islands* in *Croatia. T*he islands have high levels of available solar insolation (1450-1600 kWh/m2/yr) and high average wind velocity [135].

In *Germany* (*Bavaria*), MAN technologie AG has been responsible for the compressed hydrogen storage allowing for a driving range of around 250 km, while Linde AG took care of the hydrogen periphery and delivers the hydrogen for the test operation scheduled for the second half of the year 2000 [136].

In *Denmark* the danish hydrogen energy programme was established in 1998, with the purpose of demonstrating concrete possibilities for hydrogen technologies in the future energy system. Research in hydrogen-related technologies such as fuel cells had already been on going for about 20 years through the Danish energy research programme [137].

At the same time, the *UK* and other national governments have entered into commitments to reduce emissions of carbon dioxide and other global warming gases under the Kyoto protocol. These commitments must be viewed against a forecast increase in use of road vehicles, coupled with the increased public awareness of the potential consequences of global warming brought about by this winter's flooding [91].

The performance of a privately owned photovoltaic (PV) hydrogen production and storage installation in a one-family house at Zollbruck i.e. in *Switzerland* has been studied [138].

A photovoltaic hydrogen energy system project was developed at *Helsinki* University of Technology [139].

In *Romania*, the hydrogen was evolved over zeolites such as: Fe-mordenite, La Ce ZSM-5, Ag ZSM-5 and Pb Zsm-5 with metalic ions located in cations positions in the channels of mordenite structure and ZSM-5 structure respectively [140].

7. Hydrogen energy systems, international conferences, concepts, organizations, periodicals, books, visual programs, internet sites, companies, applications of hydrogen

It was agreed that the Hydrogen Energy System was an idea whose time had arrived. It was the permanent solution to the depletion of conventional fuels. It was the permanent solution to the global environmental problems [141] (Fig. 8).

One of the first activities of the International Association for Hydrogen Energy was

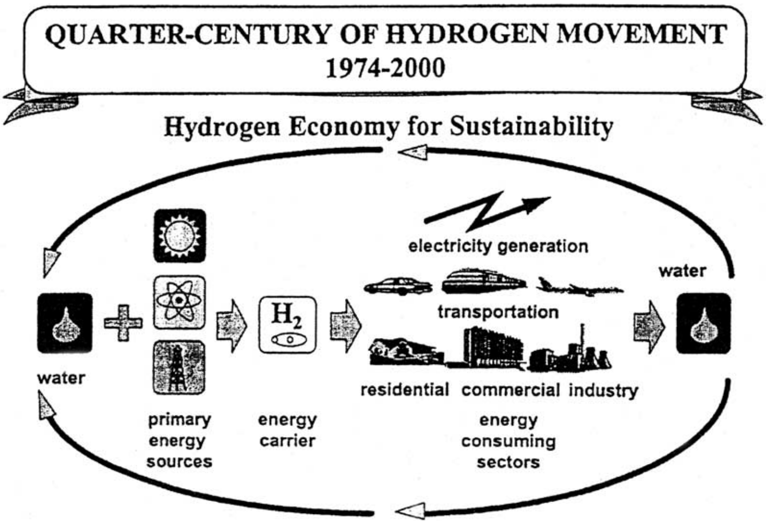

Fig. 8. A schematic diagram of the hydrogen energy system.

to organize the biennial World Hydrogen Energy Conferences (WHECs) to provide a platform for Hydrogen Energy community (Fig. 9).

Today the words : “Hydrogen Energy”, “Hydrogen Economy”, “Hydrogen Energy System” are well known and accepted (Fig. 10).

Twenty five years ago, there was no organization dedicated to hydrogen energy. Today, national and international organizations, devoted to hydrogen energy cover the globe. As can be seen in Fig. 11, there are at least eighteen such organizations.

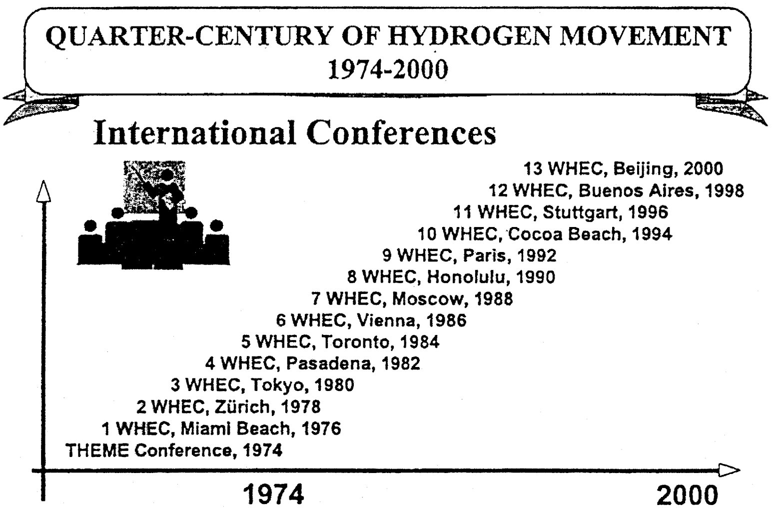

Fig. 9. International conferences on hydrogen energy.

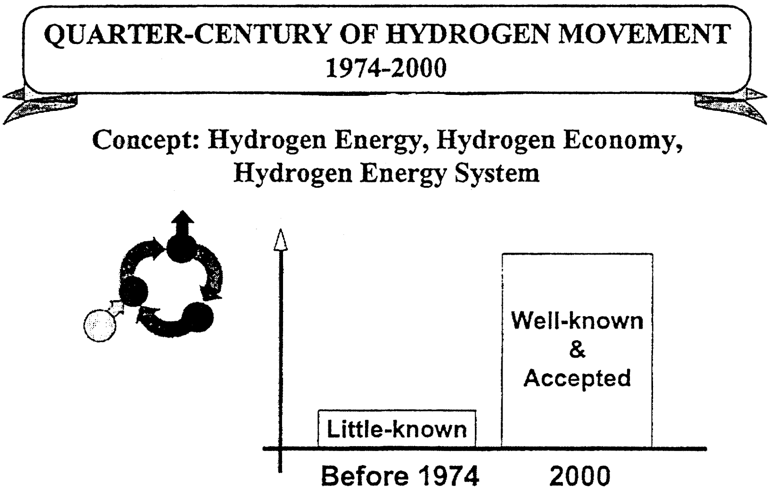

Fig. 10. Acceptance of "hydrogen energy", "hydrogen economy", "hydrogen energy system" concepts.

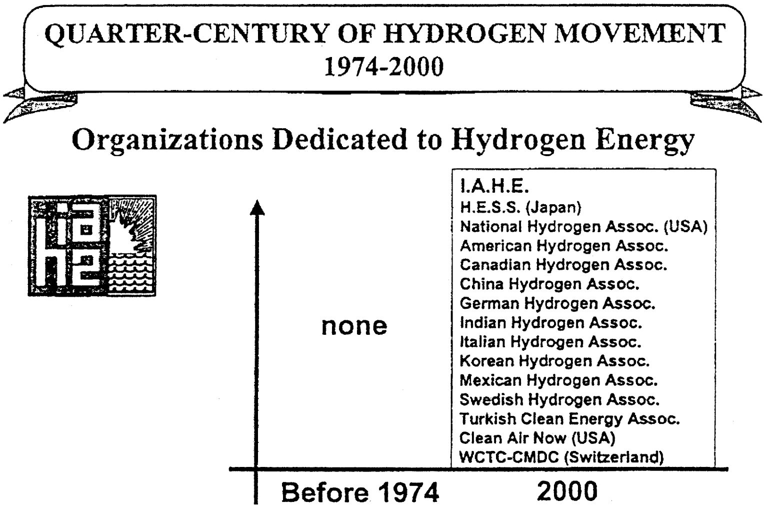

Fig. 11. Organizations dedicated to hydrogen energy.

In Fig. 12 the most important periodicals on hydrogen are presented.

The number of hydrogen energy-related books has shown an exponential growth over the past 25 years (Fig. 13).

Many imaginative and popular programs aand documentaries have been produced by major television companies, hydrogen energy organizationss, and companies working on the hydrogen energy technologies (Fig. 14).

There are a lot of internet sites which are dedicated to giving information on Hydrogen Energy. Their number are growing fast (Fig. 15).

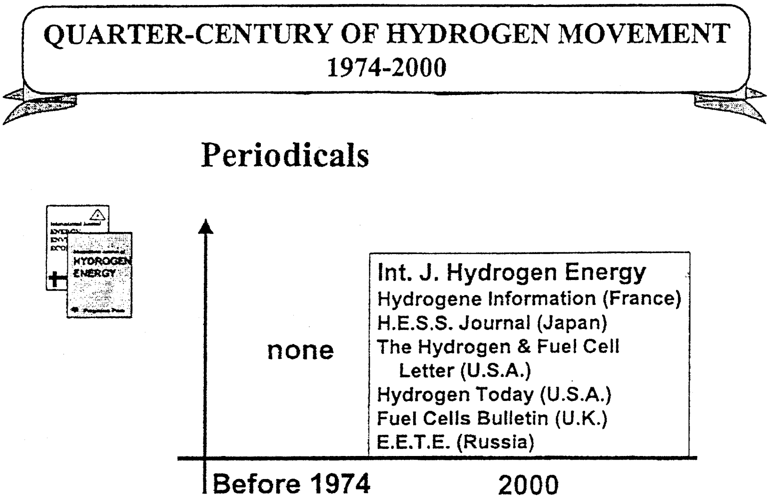

Fig. 12. Periodicals on hydrogen energy.

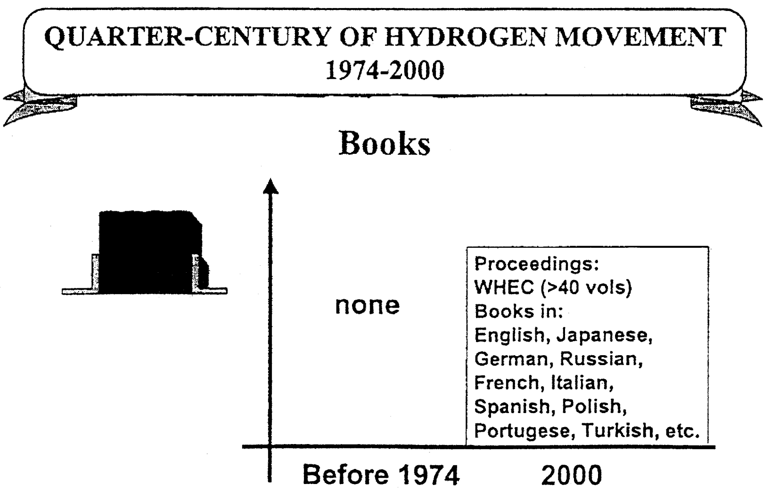

Fig. 13. Books on hydrogen energy.

Major power generating equipment manufacturers have become involved in research, development, and marketing of hydrogen fuel cell power plants. Several new companies have been formed specifically to work on fuel cells (Fig. 16).

All of the major car companies of the world are now involved in the development and commercialization of hydrogen-fuelled motor vehicles. Most of these companies are preparing to offer hydrogen-fuelled cars in 2004 (Fig. 17).

The Navy has decided to have its next generation of submarines incorporate hydrogen fuel cell power plants (Fig. 18).

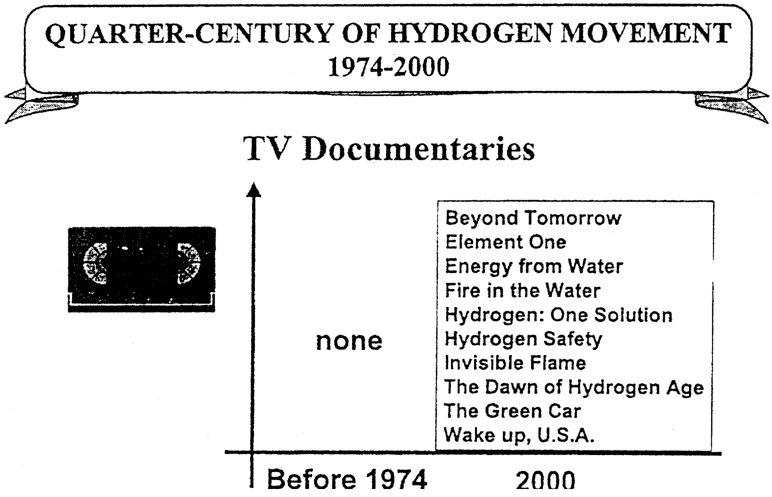

Fig. 14. Visual programs on hydrogen energy.

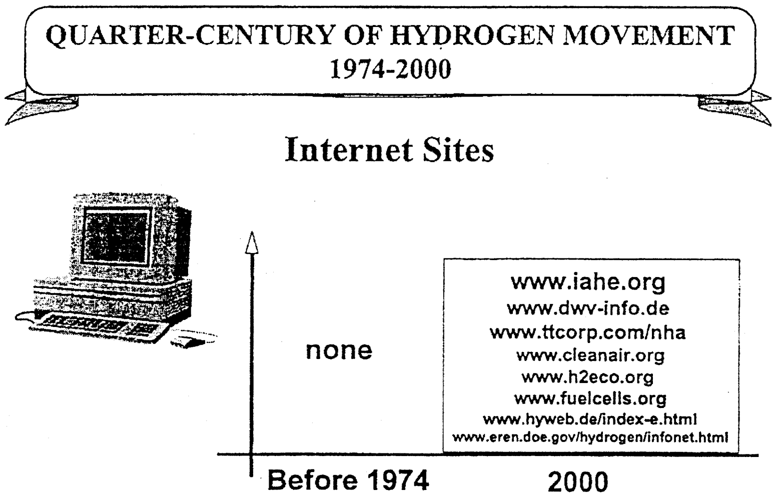

Fig. 15. Internet sites on hydrogen energy.

Before 1974, hydrogen was used in rockets by the Soviet and United States space programs. Now, the other countries are using hydrogen as the staple fuel of their space programs because of another unsurpassed, unmatched property of hydrogen—that of being the lightest fuel (Fig. 19).

Before 1974, there were no aerospace planes, which of course would have used hydrogen as fuel, because it is the fuel of choice for space programs. Today, we have the American shuttle visiting space, putting communication satellites and observation satellites in orbit, conducting various scientific experiments, and carrying the parts

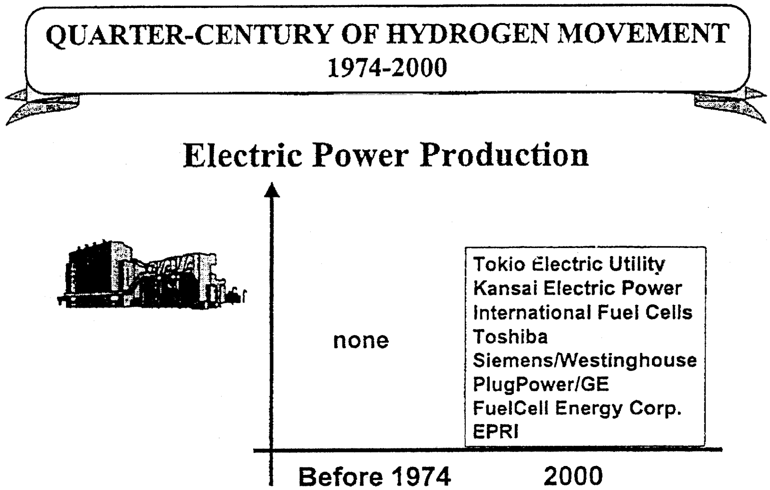

Fig. 16. Companies and organizations involved in hydrogen fuel cell electric power generation.

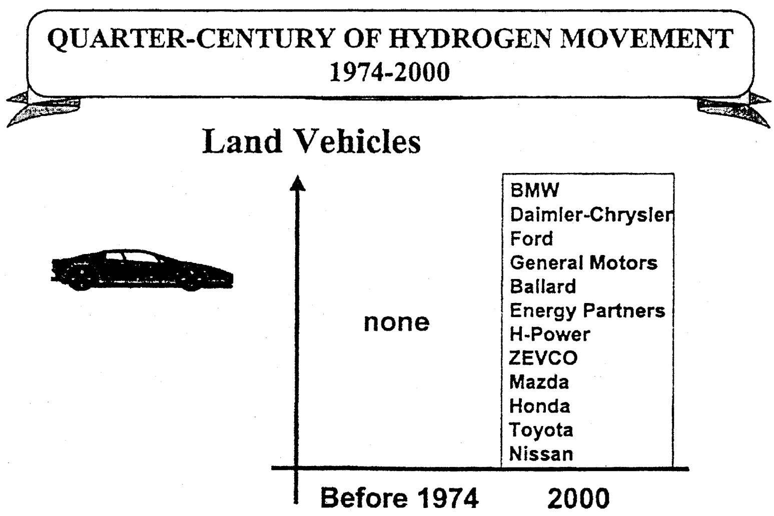

Fig. 17. Companies involved in hydrogen fuelled vehicles.

of the international space station. Russia has built a shuttle that can land automatically without a pilot being in charge. The European two plane Sănger System is on the drawing board. US Space Organization NASA is developing a single stage to orbit aerospace plane, named "VentureStar" to replace the present shuttle (Fig. 20).

The contractors are Lockheed-Martin and Rocketdyne, a division of Boeing. It will use an aerospike rocket engine expected to run on "slush hydrogen"—a mixture of liquid and solid hydrogen which makes use of another unique property of hydrogen, resulting in the reduction of storage size. The companies are now working on

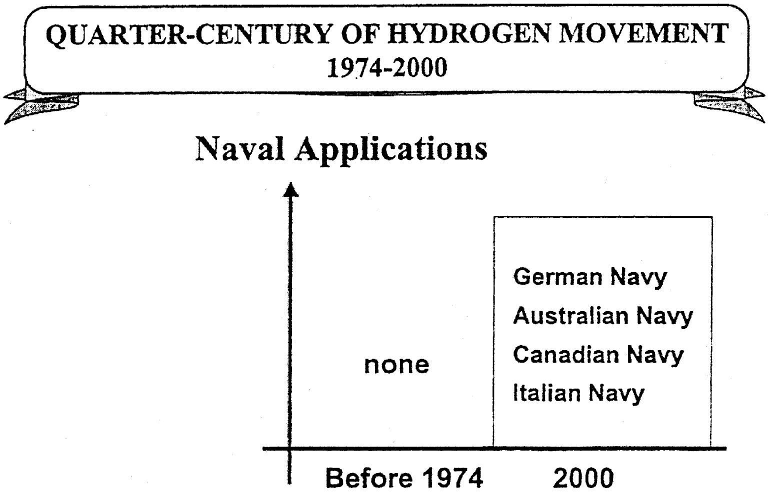

Fig. 18. Naval applications of hydrogen.

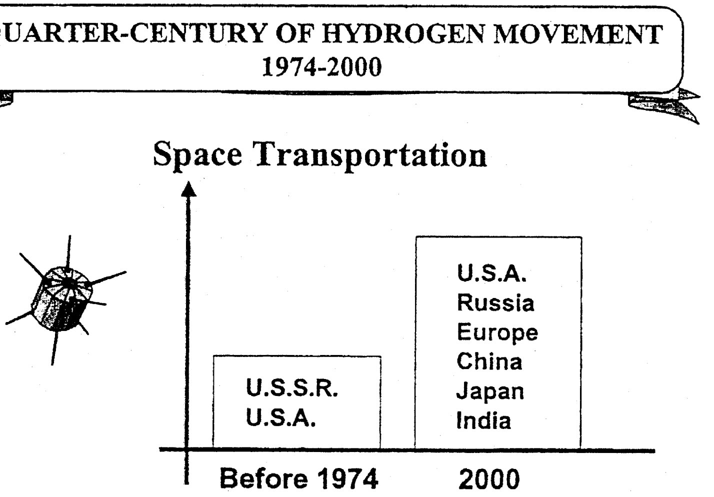

Fig. 19. Hydrogen in space programs.

a one-third size concept demonstrator named X-33, which is scheduled to fly in 2002. There is no doubt that the experience gained will be of immense value in building tomorrow's hypersonic passenger transport of course, to be fuelled by hydrogen.

Because of its light weight and excellent combustion characteristics, hydrogen is the ideal fuel for airplanes. In 1956, a Pratt & Whitney developed hydrogen-fuelled turbo jet engine was mounted on one side of a B-57 bomber and some in-flight data were collected. After 1974, hydrogen-fuelled airplane activities have increased (Fig. 21).

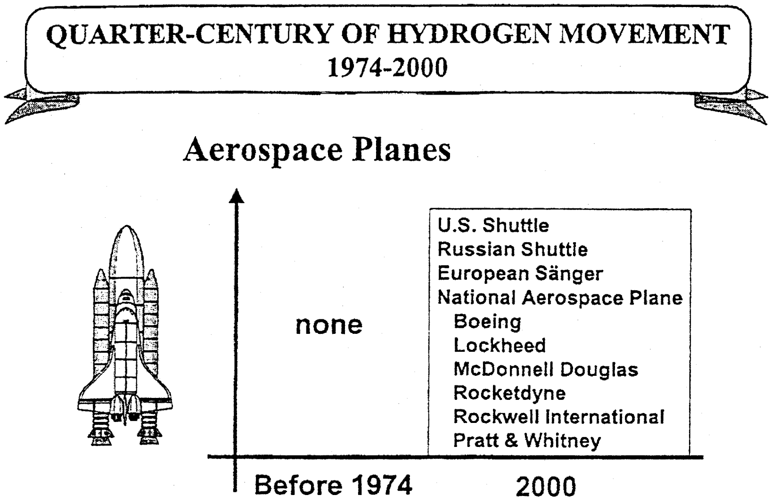

Fig. 20. Hydrogen in aerospace planes.

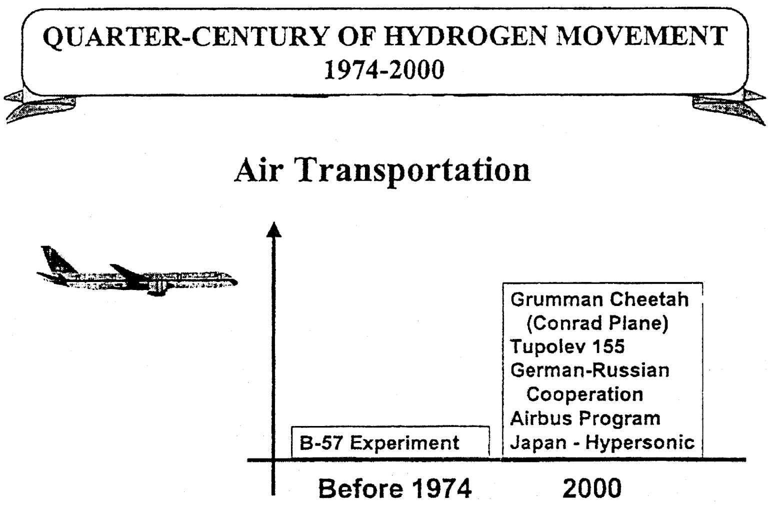

Fig. 21. Hydrogen in air transportation.

On April 15, 1988, the first passenger plane flew on a hydrogen-fuelled engine near Moscow. The Tupolev 155 (equivalent to an American Boeing 727) was equipped with two engines one running on hydrogen, the other on jet fuel—a liquid hydrogen storage tank, and a hydrogen supply and control system. The plane took off and landed on jet fuel, but hydrogen was used during the cruising phase of the flight. The various aeronautical establishments of Russia and Tupolev Institute are now working on the design and development of an all-hydrogen supersonic passenger plane, which will be called the Tupolev 204.

On June 17, 1988, two months after the flight of the Soviet jet, Bill Conrad, a retired Pan American pilot, flew a hydrogen-fuelled single engine plane in Fort Lauderdale, FL. The flight lasted only 36 s, but the fact that it was fuelled entirely by hydrogen in take-off, flight and landing established a new record.

Actually, Mr. Conrad's plan was to taxi down the runway to the starting point, then take off, fly a few times above the airport and land, all on hydrogen fuel. Because hydrogen fuel is more efficient than conventional fuel, the plane suddenly lifted off the ground while taxiing. Mr. Conrad immediately reduced power, put the plane back on the runway, continued in his taxiing mode to the starting point, ready for the flight. The officials from the Civil Aeronautics Board and other recording agencies told Mr. Conrad that he had already established a record and there was no need for him to fly again.

The European Airbus Company has initiated a program of research and development work for a hydrogen-fuelled air transport. Their studies indicate that although hydrogen costs more than jet fuel, the airfares for hydrogen-fuelled air transportation would be competitive with today's airfares, because of the great weight and energy savings with (the much lighter) hydrogen fuel. Germany and Russia have signed an agreement of cooperation for the development of hydrogen-fuelled air transportation. Japan has initiated research and development work on a hypersonic transport, for which hydrogen is expected to be the fuel of choice, because of its excellent combustion properties, light weight and environmental compatibility.

One of the unique properties of hydrogen is that it will combine with certain metals and alloys easily, in large amounts, forming hydrides in exothermic chemical reactions. When hydrides are supplied with heat, hydrogen is released. The temperature and pressure characteristics vary for different metals and alloys. Advantage is being taken of these properties for many electrochemical and thermochemical applications (Fig. 22).

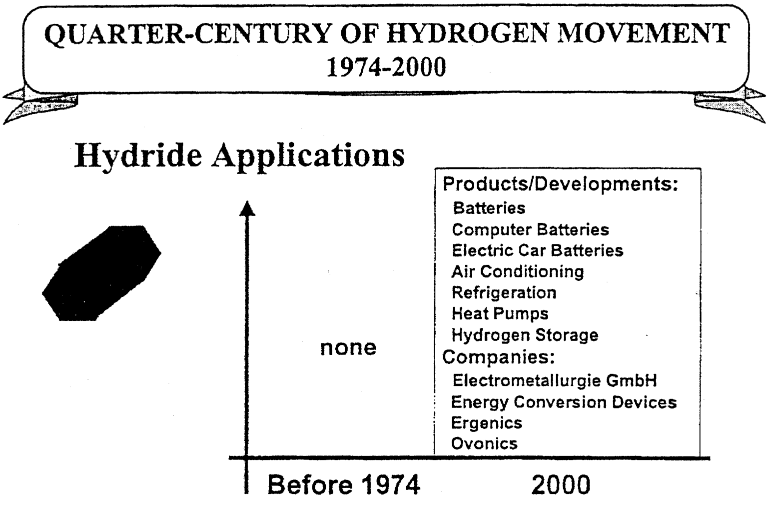

Fig. 22. Hydrogen hydride applications.

Smaller size hydrogen hydride batteries (e.g., for lap top computers), and larger batteries for electric cars have already been commercialized.

There are demonstration projects for hydrogen-hydride air conditioning, refrigeration and heat pumps. They do not need chlorofluorocarbons, and as such, they will not damage the ozone layer. Conversion to hydrogen-hydride air conditioning and refrigeration systems will put a definite stop to the ozone layer depletion.

Another unique property of hydrogen is the flameless combustion or the catalytic combustion in the presence of small amounts of catalysts, such as platinum or palladium. Catalytic combustion applications have many advantages over those of flame combustion applications: They are safer and have higher second law efficiencies, as well as being environmentally compatible. Many residential and commercial appliances have been developed using this unique property of hydrogen (Fig. 23).

Today the German/Saudi Arabian Hy-Solar Project is producing solar hydrogen in the world's largest petroleum country. Saudi Arabians expect eventually to be the permanent exporters of energy in the form of solar hydrogen and they are preparing for it.

Euro-Quebec is another successful international program. They have been looking into applications of relatively inexpensive hydro power-produced liquid hydrogen imported to Europe from Canada—applications such as for city bus transportation and smelting of iron, as well as the development of an infrastructure for overseas transportation and storage of liquid hydrogen. Norway and Germany are working on a similar program.

The Japanese WE-NET Program is the most ambitious and comprehensive hydrogen program in the world. Japan expects to spend about 4 billion dollars by 2020 to achieve what amounts to a deliberate and planned way for conversion to hydrogen.

The International Space Station, which is now under construction, uses hydrogen

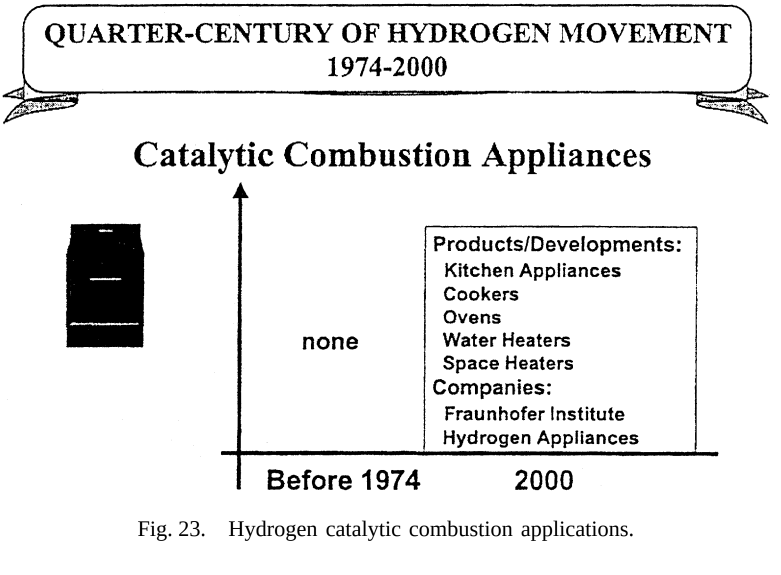

Fig. 23. Hydrogen catalytic combustion applications.

for transportation, which will use hydrogen fuel cells to provide electricity and potable water, is another important international program based on hydrogen energy. Planning for the United Nations Industrial Development Organization's International Centre for Hydrogen Energy Technologies (to be established in Istanbul, Turkey) is moving ahead (Fig. 24).

Of course, no technology can take roots without standards, and no universal technology can be established without international standards. In 1990, the International Standards Organization, based in Geneva, Switzerland (which is now an affiliated organization of the United Nations), with the initiative and representations of Gustov Grob of Switzerland, decided that the time had arrived for preparing international standards for hydrogen energy technologies. They established a committee, ISO/TC-197 Committee, to prepare such standards. During its first meeting, the Committee formed 10 sub-committees to work on the standards for Hydrogen Energy Technologies (Fig. 25).

It is gratifying to note that the committee's work is successfully moving ahead.

As you can gather from this overview, during the past quarter of a century, the fundamentals of the Hydrogen Energy System have been worked out, and strong foundations have been laid. As we enter the 21st Century, the development and commercialization of the various components of the Hydrogen Energy System are being accelerated. Our studies show that the world economy would essentially be based on Hydrogen Energy towards the end of the forthcoming three-quarters of a century, i.e., by 2074 (Fig. 26).

8. Conclusions

Hydrogen Energy has moved forward on all fronts; making in-roads in all areas of energy.

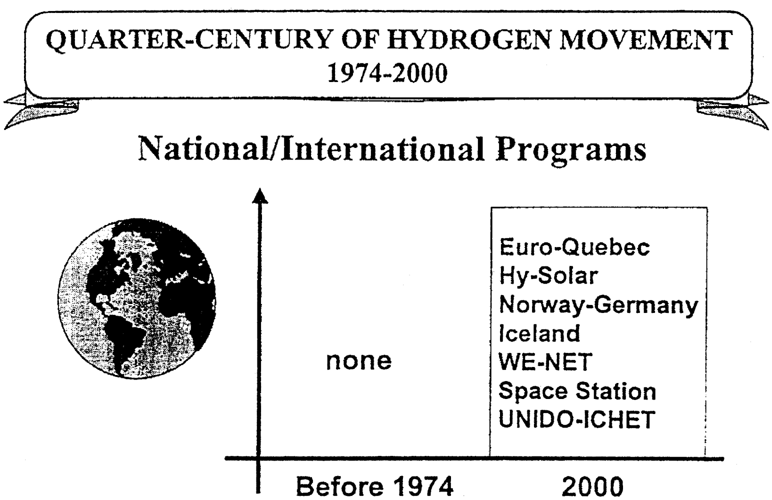

Fig. 24. Hydrogen energy international programs.

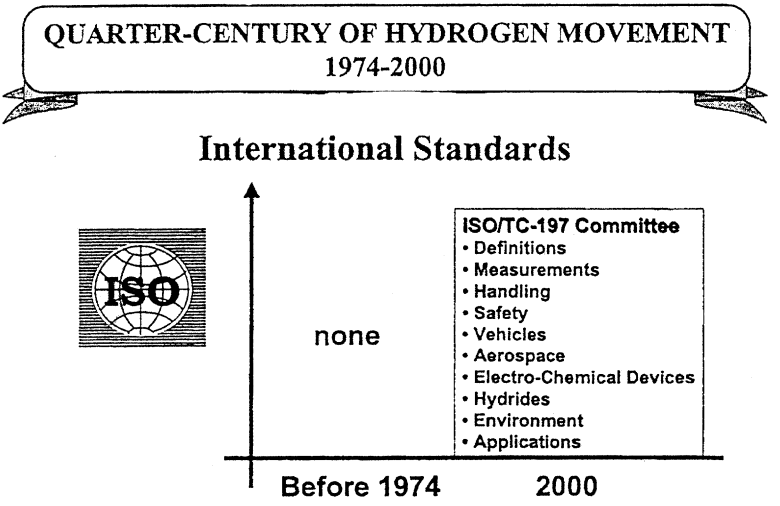

Fig. 25. International standards for hydrogen energy technologies.

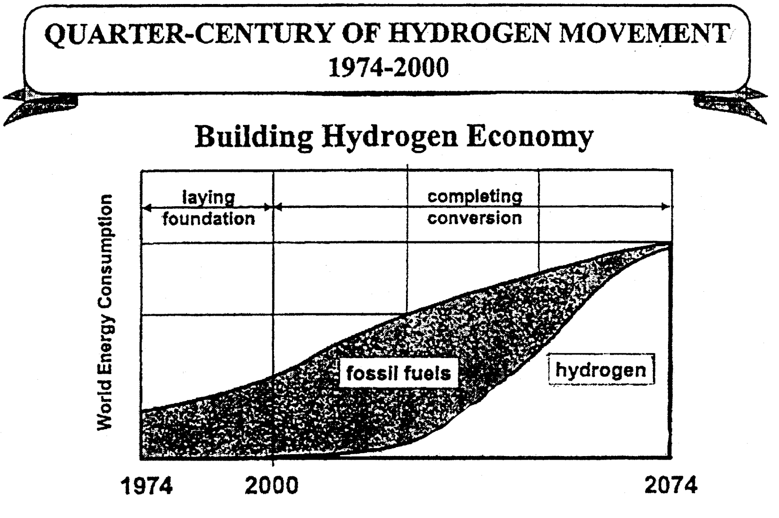

Fig. 26. Building hydrogen economy.

We have much to accomplish if we are to realize our goal of establishing hydrogen as the fuel to power the world economy. The developments prove that we are making significant progress. Westinghouse announced that it will start offering commercially solid oxide hydrogen fuel cell power plants to utilities starting next year. The bus manufacturers will have hydrogen-fueled buses on the market by the year 2003. Major car companies will begin selling hydrogen fueled cars around 2004. Several solar hydrogen demonstration plants have been built. Other major hydrogen projects are moving ahead. The development of the international standards for hydrogen

energy is moving ahead. Hydrogen production, storage and utilization technologies are continually improving. It is only a matter of time before hydrogen will start replacing fossil fuels on a large scale.

Once the hydrogen story is known, the transition to our new economy will progress rapidly. The future for our planet is bright because hydrogen provides the solution to environmental pollution and dwindling fossil fuels. On the transition path from fossil fuels to hydrogen, the economy will prosper. The fossil fuel infrastructure will remain in place without loss of jobs, but a change only in job descriptions, as this infrastructure becomes the hydrogen infrastructure. Energy investors will prosper [142].

9. Introduction to references

The different approaches for splitting of water in hydrogen and oxygen have been summarized in Ref. [4].

Solar hydrogen provides the link between the pre-industrial solar era, the first solar civilization, which only knew of stored solar energy in the forms of biomass and hydropower, and a post-fosil era, the second energy in the solar civilization [7,8].

The worldwide photovoltaics market has grown rapidly in recent years. This is detailed in Ref. [9].

The natural cycle of hydrogen-water is reported in Ref. [10].

Development of the solide electrolytes in water electrolysis for hydrogen production is important [15].

A thermal process for hydrogen generation has been developed using water in the presence of zeolites impregnated with non-noble metals of variable valences and activated in vacuum [50]. This work was succesfull continued and recently was reported that hydrogen evolved in thermal decomposition over zeolites was of the highest value when the HCl aqueous solution was added [51].

The criteria for the selection of the thermochemical cycles used to establish the maximum efficincy for multi-step water splitting have been analyzed [53].

Studies concerning solar global radiation and the value of relative sunshine are relevant for solar energy stored in hydrogen [56].

The field of photocatalysis has been expanding rapidly in connection with light energy, especially in the conversion of solar energy to chemical energy using solid catalysts such as TiO_2 [60]. The influence of altervalent cation doping of TiO_2 on its performance as a photocatalyst in water cleavage has been investigated [62]. Also photocatalytic decomposition of water into hydrogen and oxygen using semiconductors loaded with various metals have been widely studied [64]. Direct conversion of solar energy into hydrogen as a storable energy carrier can in principle be achieved by photoelectrochemical means. High efficiencies have been obtained in laboratory solar cell [79].

Photosynthetic bacteria represent a futuristic aproach with extent on light conversion efficiency [80].

Refs. [96–99,101,103–106] are also of special interest for hydrogen storage.

Ref. [111] deals with the effective costs of fuels.

Substituting hydrogen for fossil fuel will result in improved physical health [113].

An excellent analysis of quarter century of hydrogen movement 1974–2000 is listed in Ref. [141].

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